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Under the SDIO/IST support (grant N00014-90-J-1761), we have made progress in the investigation of the metal systems that are thermodynamically stable on GaAs. Successful growth of the single phase $PtGa_2$ and CoGa on GaAs has been demonstrated by MOCVD (metal organic chemical vapor deposition) using mixed-metal organometallic precursors of limited volatility and by MBE (molecular beam epitaxy). Fundamental understanding of these thermodynamically stable compounds has been obtained. Our accomplishments include the studies of the stability, the growth process, the chemical, physical, and electrical properties of metal/GaAs systems.

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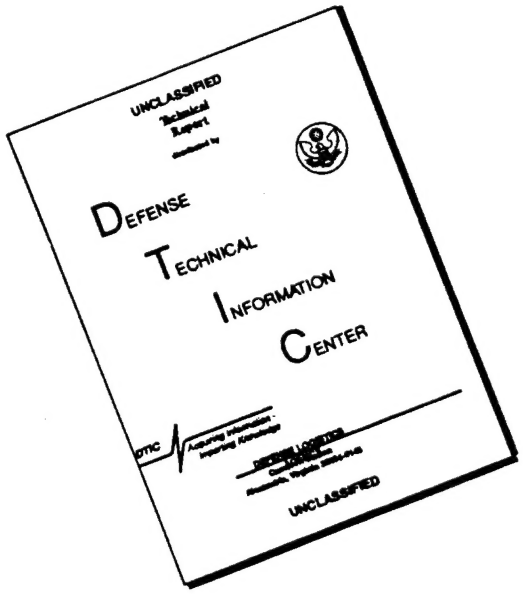

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Final Technical Report

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Epitaxial Growth and Electro-Optical Properties of Metal GaAs Superlattices

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Epitaxial Growth and Electro-Optical Properties of Metal GaAs Superlattices

Under the SDIO/IST support, we have made progress in the investigation of the metal systems that are thermodynamically stable on GaAs. Successful growth of the single phase $PtGa_2$ and CoGa on GaAs has been demonstrated by MOCVD (metal organic chemical vapor deposition) using mixed-metal organometallic precursors of limited volatility and by MBE (molecular beam epitaxy). Fundamental understanding of these thermodynamically stable compounds has been obtained. Our accomplishments include the studies of the stability, the growth process, the chemical, physical and electrical properties of the metal/GaAs systems.

In the MOCVD approach, we have made a substantial progress and obtained a great deal of information about how to deposit high purity and high quality metal and intermetallic films. For example, using hydrocarbon ligands under H_2 ambient, we have obtained Pt metal films purer than those obtained from vacuum deposited films from a high purity source. The presence of H_2 enables the deposition to occur at a low temperature (120 - 200 C) and thus prevent carbon contamination due to the graphization at temperature about 450 C. Thus far no fully hydrocarbon complexes are available, but similar process is expected of CoGa and NiAl deposition. More significantly, the UV photo-assisted experiments have demonstrated that UV assisted deposition results a selective seeding of the growth in the presence of H_2. The latter suggests the possibility of the selective growth and in-situ fabrication of the quantum wires and dots using the photo-assisted seeding by a laser beam.

In the MBE approach, two different orientations (100)CoGa and (110)CoGa on (100)GaAs are always observed in the beginning of our research, which is a common problem in the deposition of intermetallic compounds on GaAs (e.g., RhGa and NiAl). However, one of our major accomplishments is to control the orientations at will by the study of the initial surface condition. In that study, the initial growth conditions are determined by the in-situ RHEED (reflection high energy electron diffraction) pattern, and for Co-terminated surface, the orientation is (100)CoGa/(100)GaAs. For Ga-

terminated surface, the orientation is (110)CoGa, and for As-terminated surface, the deposition is the mix of (100) and (110)CoGa. The good quality of the epitaxial films is characterized by RHEED, RBS (Rutherford backscattering) and X-ray rocking curve. Both the (100) and (110)CoGa show a streaky RHEED patterns with clear Kikuchi bands. The RBS channeling minimal is only 8% and the FWHM (full width half maximum) of the X-ray rocking is only 0.2 degree.

Both the CoGa and the $PtGa_2$ contacts on GaAs show a sharp interface and good crystallinity up to 800 C annealing. For example, phase stability versus the lattice mismatch of (100)$Co_{1-x}Ga_x$ thin films on GaAs has been studied. The results indicated that this contact is thermochemically stable on GaAs for annealing in an open system to 800 C for x=0.61, which corresponds to 0% lattice mismatch of the film with the substrate. This is presently one of the most stable epitaxial metallization of GaAs. We have also shown the significantly increased phase stability of the perfectly lattice-matched films with respect to films that have 2% lattice mismatch.

In order to grow a GaAs/metal/GaAs quantum well structure, it is essential to have a smooth, continuous metal thin film on GaAs, in addition to have a thermochemically stable interface. This property was verified in our study of electrical resistivity of ultrathin, epitaxial CoGa film on GaAs. Transport studies were performed in the temperature range of 4 to 300 K for layer thickness from 10 to 730 A, and all the films were found to be electrically continuous. The result indicates that the defects and impurities level are comparable to the bulk metal.

Another interesting characterization work that we have done is the measurements of SBHs (Shottky Barrier Height) of the CoGa on GaAs contacts. Macroscopically, the Schottky barrier formation of the CoGa on n-(100)GaAs was investigated by I-V, C-V, and IP(internal photo emission). The SBHs are different for different CoGa phases, indicating that the mechanisms of the barrier formation for these phases are different. Since the phase of CoGa film is controllable, this result demonstrates a new method to vary the SBH of GaAs diodes, and may help us understand further about the Fermi level pinning problem. The temperature dependence of the Schottky barrier height is also examined and the result shows that the Fermi level is pinned to a fixed level with respect

to the GaAs conduction band minimum regardless of the value of the SBH. In addition, the barrier height is found to be constant from 150 to 300 K for each of the phases. On the other hand, microscopic study of the SBHs with an extremely high spatial resolution was also performed by BEEM (ballistic-electron-emission microscopy). In this study, the energy levels corresponding to electron transmission from CoGa layer into the three conduction bands minima of GaAs were measured. The result confirms that (100)CoGa / n-(100)GaAs has a lower SBH than (110)CoGa. Further, it has been found that (100)CoGa / n-(100)GaAs has a uniform SBH with a lateral variation less than 100 mV, but (110)CoGa / n-(100)GaAs has a much less uniform SBH with a lateral variation as large as 380 mV, possibly due to the lattice mismatch at the interface.

(a.) Published Papers in Referred Journals

R. Arghavani, R. P. G. Karunasiri, T. C. Kuo, Y. K. Kim, and K. L. Wang: "Internal photoemission in CoGa/GaAs Schottky barriers, possible injection of electrons into L valleys," Journal of Vacuum Science & Technology A9(3), 987 (1991).

T. C. Kuo, T. W. Kang, and K. L. Wang: "RHEED studies of epitaxial growth of CoGa on GaAs by MBE-determination of epitaxial phases and orientations," Journal of Crystal Growth 111, 996 (1991).

D. A. Baugh, A. A. Talin, R. S. Williams, T. C. Kuo, and K. L. Wang: "Phase stability versus the lattice mismatch of (100)$Co_{1-x}Ga_x$ thin films on (100)GaAs," Journal of Vacuum Science & Technology B9(4), 2154 (1991).

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F. Maury, A. A. Talin, H. D. Kaesz, and R. S. Williams: "Epitaxial growth of CoGa on GaAs by organometallic chemical vapor deposition," Chemistry of Materials 5(1), 84 (1993).

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Internal photoemission in CoGa/GaAs Schottky barriers, possible injection of electrons into the *L* valley

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Internal photoemission in epitaxially grown films of CoGa/GaAs Schottky barriers by back illumination is used to study the injection of electrons into L and X valleys of the conduction bands of n-type GaAs. The general theory of Fowler predicts that the photocurrent per absorbed photon should vary as the square of the photon energy $h\nu$ for $[(h\nu - \Phi_b/kT)] \geqslant 0$, where Φ_b is the difference between the Fermi level and Γ point in the GaAs conduction band. Unlike the case for Au/GaAs Schottky barriers, we observe two thresholds in the photocurrent measurements of uniform epitaxial CoGa/GaAs contacts. The second threshold formed at ≈ 0.3 eV higher than the first threshold (Γ point) is interpreted as the injection of carriers into the L valley of the GaAs from the metal side. A third threshold at ≈ 0.5 eV above the Γ point requires a photon energy greater than the energy gap of GaAs (1.4 eV) and hence cannot be observed in the back illumination mode.

I. INTRODUCTION

Despite decades of intensive research on metal/semiconductor contacts the details of these Schottky barrier contacts are not yet well understood. Although the Schottky–Mott theory explains the fundamental mechanism by which the barrier height forms in ideal metal/semiconductor contacts, the insensitivity of this barrier to the work function of the metal led Bardeen to suggest Fermi-level pinning due to intrinsic surface states present on the semiconductor surface.[1] The "Bardeen limit" seemed to give a satisfactory description of the barrier height formation, yet the apparent pinning of the Fermi level on such Schottky barriers appears not to support the Bardeen theory for this case due to the lack of intrinsic surface states in the GaAs (110) surface.[2,3] This has led many researchers to search for the source of Schottky barrier height formation in nonuniform interface or Fermi-level pinning due to interface defects. Among the leading theories are: (a) the metal-induced gap states (MIGS),[4] where it is assumed that the tail wavefunction of the metal conduction electrons tunnels into the semiconductor energy gap forming extra states in the gap that would pin the Fermi level, or (b) the unified defect model,[5] in which it is assumed that electronic states in the energy gap of the semiconductor are caused by intrinsic atomic vacancies (defects) on the surface of the semiconductor, or (c) the effective work function model,[6] where the work function of the metal is replaced by an effective work function which takes into account the different work functions of the microclusters formed from chemical and/or other effects at the interface following metal deposition. A majority of attention has been given to the study of the quality of the interface rather than the surface states in metal/semiconductor contact theory. The lack of thermodynamically stable elemental metals on GaAs has led many to look for intermetallic compound metals to metal contacts GaAs. CoGa for example, is a thermodynamically stable compound metal that can be epitaxially grown on GaAs.[7,8] Although details of the interface quality and abruptness are relatively unknown, it is generally believed that unlike element metals, CoGa will not interact with GaAs. Furthermore, the lattice constant of $Co_{1-x}Ga_x$ can be adjusted so that it equals half of the GaAs lattice constant. Using this adjustment uniform CoGa epitaxial films can be grown on GaAs, thus reducing the dislocations at the interface. This would further improve the reproducibility of good electrical characteristics of such Schottky diodes. On the other hand gold has been shown to diffuse through GaAs as seen in XPS studies which show that even for thick (>200 Å) overlayers of Au or Al on GaAs, As or Ga will diffuse outward toward the surface.[9]

Internal photoemission (where the electrons are photoinjected from the metal side to the conduction band of the semiconductor) is a well-established technique for the determination of the barrier heights in metal–semiconductor contacts.[10] Under the assumptions that (a) the transition rate, or the matrix element, for the interaction of the electromagnetic field with the conduction electrons of a metal near the photoelectric threshold is independent of the photon energy, (b) the conduction band for the metal has a parabolic density of states, and (c) only the photogenerated electrons with kinetic energy normal to the interface greater than or equal to the barrier height are transferred to the semiconductor, the number of photoelectrons emitted to a semiconductor from the metal contact is given by:[11]

$$N = \frac{2\sqrt{2}}{h^3}\pi(m)^{3/2}\frac{1}{(\Phi_b + E_f - h\nu)^{1/2}}k^2T^2 f_1(\mu), \quad (1)$$

where $f_1(\mu) = e^{\mu} - \frac{1}{2}e^{2\mu} + \frac{1}{3}e^{3\mu} - \ldots, \mu = (h\nu - \Phi_b)/kT$ and Φ_b is the Schottky barrier height. For our case of interest, where $h\nu > \Phi_b$:

$$N = \frac{2\sqrt{2}}{h^3}\pi(m)^{3/2} \times \frac{1}{(\Phi_b + E_f - h\nu)^{1/2}}k^2T^2\left[\frac{\pi^2}{6} + \frac{\mu^2}{2} - f_2(\mu)\right]. \quad (2)$$

Here, $f_2(\mu) = e^{-\mu} - \frac{1}{2}e^{-2\mu} + \frac{1}{3}e^{-3\mu} - \ldots$. For the case

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RHEED studies of epitaxial growth of CoGa on GaAs by MBE – determination of epitaxial phases and orientations

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Epitaxial growth of single crystal CoGa is investigated in-situ using reflection high energy electron diffraction (RHEED). The formation of different phases of CoGa (different stoichiometric compounds and epitaxial orientations) due to various initial growth conditions has been probed with X-ray diffraction and correlated with the RHEED patterns. The growth of (100)CoGa or (110)CoGa is found strongly dependent on the termination of the GaAs surface, with either Co or Ga, before the epitaxial deposition of CoGa. When the flux ratio is deviated from the proper stoichiometric range, additional Co–Ga–As compounds are found in the X-ray diffraction measurement. It is concluded that the CoGa phases and orientations can be determined by pre-deposition of Co or Ga with a control of stoichiometry in the proper range. The high quality epitaxial CoGa has potential applications in thermodynamically stable contacts, and more importantly for fabrication of GaAs/metal/GaAs quantum well structures.

1. Introduction

Thermodynamically stable metal contacts on GaAs are very important for both Ohmic and Schottky contacts. Since only W and Mo in the element metal form do not react with GaAs, intermetallic compounds have attracted great deal of interest in the past few years [1]. These intermetallic compounds, such as CoGa [2], RhGa [3], NiAl [4], and NiGa [5], have a CsCl structure and the lattice constants are close to half of the lattice constant of GaAs. Thus, epitaxial deposition of these intermetallic compounds on GaAs is plausible.

CoGa has certain advantages which make it a good candidate for metal contact on GaAs. First, there exist only two stable phases of Co/Ga compounds, which are CoGa and $CoGa_3$ [6], and this makes it easier to control the growth of single phase CoGa on GaAs. Second, the stoichiometry of $Co_{1-x}Ga_x$ can be varied from 31% to 62% [7], and this flexibility of stoichiometric variation makes the flux ratio control less critical. Furthermore, the lattice mismatch of different stoichiometric CoGa's with GaAs (half of the lattice constant), varies from 1.8% to 0.5% as Ga content is adjusted from 31% to 61% [8]. In bulk $Co_{1-x}Ga_x$, electric and magnetic properties are known to depend on the stoichiometry [9–11]. However, the properties of epitaxial $Co_{1-x}Ga_x$ on GaAs are still relatively unknown. Recent studies by Baugh et al. [12] have shown that the Ga rich condition may be thermodynamically more stable than the Co rich condition. Palmstrøm et al. [2] have demonstrated the growth of CoGa on GaAs and observed the surface reconstruction using reflection high energy electron diffraction (RHEED).

In this paper, we demonstrate the control of growth of single phase CoGa on GaAs and the epitaxial orientation in molecular beam epitaxy (MBE), by controlling the initial growth condition with in-situ RHEED diffraction.

2. Experimental

The substrate used in this study was undoped semi-insulating (100)GaAs. The wafer was first degreased, etched in $H_2SO_4 : H_2O_2 : H_2O = 8 : 1 : 1$

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Phase stability versus the lattice mismatch of (100)$Co_{1-x}Ga_x$ thin films on (100)GaAs

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Thin films of the intermetallic compound $Co_{1-x}Ga_x$, which has a broad homogeneity range and a continuously variable lattice constant, were grown on the (100)GaAs surface by molecular beam epitaxy. The stoichiometry of the films and the cleanliness of the substrates were determined *in situ* by Auger electron spectroscopy. The identity and orientation of the phases present in the films were determined *ex situ* by x-ray diffraction (XRD). The films were annealed to various temperatures in N_2 and reexamined by XRD to detect any chemical interactions between the $Co_{1-x}Ga_x$ and GaAs. Films of $Co_{1-x}Ga_x$ deposited with a 2% lattice mismatch ($x = 0.5$) reacted with the substrate to produce $CoGa_3$ at 600 °C, whereas films with no detectable mismatch ($x = 0.61$) did not react until they had been heated to 800 °C.

I. INTRODUCTION

The metal/semiconductor (M/S) interface is interesting for both chemical and physical reasons. From a chemical perspective, the bonding at an interface between a metallic and a covalent material could be intermediate between these two extremes, or it could be completely new and unique to this type of interface. Since solid/solid (S/S) reactions begin at the interface, it is important to understand what type of bonds are formed at the interface and, as a consequence, how such interface bonds affect the course of a particular (S/S) reaction. The transport of charge carriers (i.e., electrons and holes) across the (M/S) interface is also of fundamental importance. Many attempts have been made in the past to correlate the height of the interface potential barrier strictly to bulk materials properties of the metal and semiconductor.[1] However, it has become clear that interface specific properties dominate the potential barrier between compound semiconductors and metal films, although whether the dominant effects are chemical or physical in nature is still a matter of intense debate.[2,3]

One approach to address these fundamental chemical and physical questions concerning the M/S interface is to fabricate a model metal–semiconductor system with an *ideal interface* that has the following properties: (i) it is structurally perfect (i.e., the M/S interface is *epitaxial*), (ii) it is thermochemically stable over a wide range of temperatures, and (iii) it allows independent control over interface parameters such as the lattice mismatch between the metal and the semiconductor. By preventing or controlling chemical reactions at the M/S interface, it should be possible to at least conceptually separate the chemical and physical contributions to potential barrier formation.

The intermetallic compound CoGa (B2 structure) on (100) GaAs, which was first reported by Palmstrom *et al.*,[4] is a system that could potentially satisfy the above criteria. The B2 structure has a cubic unit cell and the GaAs lattice constant is close to twice that of CoGa. The work of Palmstrom *et al.* demonstrated that the CoGa/GaAs system nearly satisfies the first criterion above. A stoichiometric CoGa film has a 1.9% lattice mismatch when considering four CoGa unit cells arrayed on the (100) face of a GaAs unit cell.[5] However, in the previous work, the CoGa was essentially regarded as a line compound. Here, we explicitly recognize that B2 phase $Co_{1-x}Ga_x$ exists over a range of compositions, and that the lattice constant of the intermetallic compound is a function of its composition. We will show that a lattice-matched film of $Co_{1-x}Ga_x$ with $x = 0.61$ on GaAs is chemically more stable than a mismatched film with $x = 0.50$, which demonstrates that interfacial chemical and mechanical properties are intimately related. The lattice-matched $Co_{1-x}Ga_x$ film yields a metal/GaAs interface that is chemically stable to 800 °C, and is thus an excellent candidate for forming the ideal interface that can be used to study potential barriers.

II. EXPERIMENTAL PROCEDURE

A schematic diagram of the molecular beam epitaxy (MBE) growth chamber is shown in Fig. 1. The Co and Ga atomic beams were, respectively, derived from a 3 kW electron beam evaporator and a boron nitride Knudsen cell. The Co and Ga beams impinged simultaneously on the substrate, which was held at 300 °C or at ambient temperature for different films. Since the sticking coefficients of both Co and Ga are essentially unity at these substrate temperatures, the film composition was determined solely by the relative flux of the two beams. The relative flux was controlled by monitoring the total flux of both Co and Ga with the quartz crystal monitor and the Co beam flux density with the quadrupole mass spectrometer. The chamber was pumped by a 220 ℓs^{-1} ion pump and maintained pressures of 5×10^{-9} and 3×10^{-10} Torr with the atomic beams, respectively, on and off. The Auger system was used to check the cleanliness of the GaAs substrate and the composition of the $Co_{1-x}Ga_x$ films, with the uncertainty in determining x conservatively estimated to be ± 0.04.

The substrates were degreased in chloroform and etched

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Electrical resistivity of ultrathin, epitaxial CoGa on GaAs

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The successful growth of ultrathin CoGa on GaAs by MBE is demonstrated. The crystalline quality of the films is verified by *in situ* RHEED, RBS, and x-ray rocking curve. Transport studies are performed in the temperature range of 4 to 300 K for layer thickness from 10 to 730 Å, and all the films are found to be electrically continuous. The Markowitz's model [Phys. Rev. B **15**, 3617 (1977)] of the electrical resistivity is applied to analyze the measured data. Finally, the specularly scattering probability of these thin films is studied using Fuchs' theory [Proc. Cambridge Philos. Soc. **34**, 100 (1938)].

Because of the need for the high speed device and circuit applications, thin metallic films have attracted more and more interest in the recent years. The ability to grow thin, continuous, and epitaxial metallic films on semiconductor is made possible by MBE (molecular beam epitaxy). However, due to the stringent requirements for a plausible metal contact on semiconductor, only a few metallic compounds can fulfill the conditions for being epitaxial on semiconductor. Previously, we have demonstrated the ability to obtain the epitaxial growth of CoGa on GaAs, as well as the control of the epitaxial direction.[1] Here, we present the first result of the transport properties of the thin CoGa films on GaAs. The quality of the films is verified by the *in situ* RHEED (reflection high-energy electron diffraction), RBS spectrum (Rutherford backscattering), and the x-ray rocking curve. Finally, the size effect of the electrical resistivity is discussed.

The films are grown on the semi-insulating GaAs substrates with a 3000 Å undoped GaAs buffer layer. The shunt resistance caused by the substrate in the resistivity measurement will be minimized in this case (especially at low temperature). The growth temperature of CoGa is 300 °C, and in order to avoid the residual As incorporating into the CoGa growth, CoGa is not deposited until the chamber pressure is pumped down to 1×10^{-9} Torr. Before the growth of CoGa, approximately one monolayer of Co is first deposited, then appropriate ratio of Co and Ga fluxes are co-deposited. The detailed discussion of the growth technique and result can be found in Ref 1. The reason for using such a low growth temperature for CoGa in the present case is to avoid the interaction of Co and GaAs at the interface, and to prevent the initial three-dimensional growth at higher temperature. From the RHEED patterns, the films grown at 450 °C show a spotty pattern for the first few layers. Under the condition of the 300 °C growth temperature, the RHEED pattern is broad when the initial layer of Co is deposited but changes into a streaky CoGa pattern after 2–3 layers of CoGa growth. One concern about the low growth temperature is the high impurity incorporation and defect concentration; however, we will prove later in the resistivity measurement that this is not a big problem. The RHEED patterns of 10 Å CoGa and 750 Å CoGa samples are both shown in Fig. 1. We can see that both patterns have streaky lines and clear Kikuchi bands indicating the good crystalline quality of both films. One 750 Å CoGa sample is characterized by RBS and x-ray rocking curve. From the aligned RBS spectrum in Fig. 2 we can see that the minimal channeling yield (χ_{min}) is only 8%. The x-ray rocking curve in Fig. 3 shows that the full width half-maximum (FWHM) is approximately 0.2 deg, and the lattice mismatch between GaAs and CoGa is only 0.6%. The stoichiometry of this film can be estimated from the mismatch and is about 60% Ga ratio.[2]

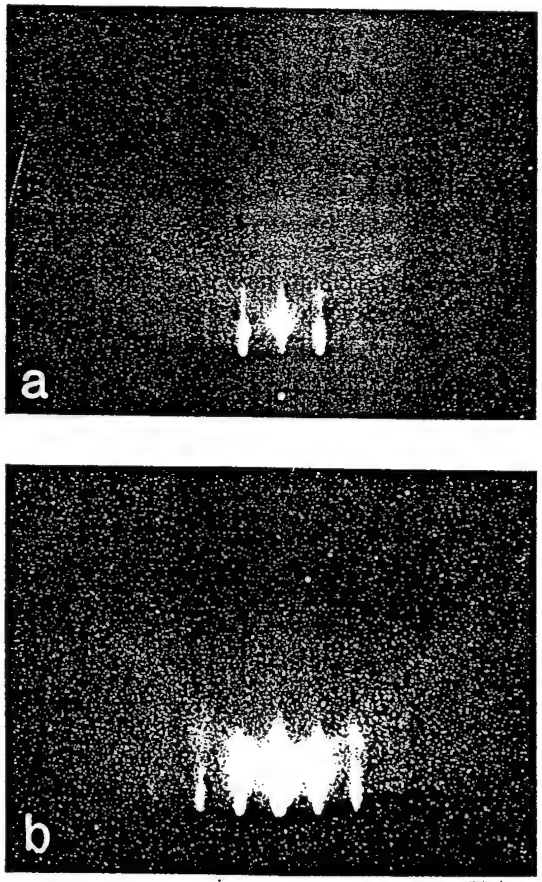

FIG. 1. RHEED patterns of the CoGa films after growth at room temperature. (a) 730 Å. (b) 10 Å. The azimuth angle is along the (011) direction.

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Interface stoichiometry dependence of the Schottky barrier height of CoGa and GaAs

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The Schottky barrier formation of CoGa on (100)*n*-GaAs is investigated. CoGa is grown by molecular-beam epitaxy, and the epitaxial orientation is controlled by the initial growth conditions of the GaAs substrate. Schottky diodes with three different phases of CoGa: (100)CoGa, (110)CoGa and mix of (100) and (110)CoGa, are fabricated and Schottky barrier heights are measured by *I–V*, *C–V*, and internal photoemission. All these three types of diodes have different values of barrier height, indicating that the mechanisms of the barrier formation for these three phases are different. The plausible mechanisms for the change of the Fermi level pinning position of these phases are discussed. Finally, the temperature dependence of the Schottky barrier height is also examined and the barrier height is found to be constant from 150 to 300 K for all of the phases.

I. INTRODUCTION

The metal/GaAs interface is an important subject for ohmic and Schottky contacts. The ability to control the Schottky barrier height (SBH) will provide advantageous manipulation in device application. However, for an ordinary metal contact on GaAs, SBH is known to pin to the mid-band gap of GaAs, independent of the metal work function. This pinning problem severely restricts the use of the Schottky diode for many device application. Since the mechanism for the pinning is not well understood yet, many theories have been proposed to explain this phenomenon. However, to date no single theory can account for all the experimental data, and new experimental results will continue to shed light on this old problem. For detailed understanding, a homogeneous interface with no reaction between the metal and GaAs is required. Recent development of the molecular-beam epitaxy (MBE) technique and the use of the intermetallic and rare-earth metallic compounds provide us with an ideal system for the study of this problem.

Although the theoretical understanding of the pinning problem is not yet clear, several novel approaches have been used to vary and control the SBH. The most common approach is to add a thin interfacial layer with different chemical or electrical properties to change the GaAs substrate surface. This layer can be a thin, counter-doping, fully depleted layer under the metal contact,[1] or a semiconductor layer such as Si,[2] or AlAs.[3] A recent method is adopted by Wu *et al.* who use a thin interfacial metal layer to adjust the SBH of the Ti/Pt/*n*-GaAs and Pt/Ti/*n*-GaAs.[4] Hirose *et al.* use a thin high-resistivity Ce-doped layer to change the SBH of Al/GaAs.[5] The interfacial layers in these novel approaches all range from a submonolayer to less than 10 Å in thickness, and the results of these works support the theory that the final Fermi level evolves over several monolayers of metal deposition. The latest report of the SBH control is by Chang *et al.*, who form the contacts at a very low temperature by Au, Cu, and Al. They claim that these various types of diodes behave close to the ideal Schottky limit.[6] Although these methods show an ability to vary the SBH, one concern here is the thermodynamic stability of these diodes. Elemental metals except W and Mo react with GaAs at elevated temperatures. For the Pt/Ti/*n*-GaAs diodes, the Pt reacts with GaAs at 500 °C.[7] Therefore, other systems are needed if devices are to go through high-temperature processes.

In this study, the intermetallic compound CoGa is chosen as the contact metal on *n*-(100)GaAs. Previously, the successful growth of epitaxial CoGa on GaAs has been demonstrated.[8] The epitaxial film gives an abrupt and reaction-free interface which is a perfect candidate to test the theoretical methods of the Schottky barrier formation. Baugh *et al.* have already demonstrated that (100)CoGa/(100)GaAs is thermodynamically stable upon annealing up to 700 °C.[9] A preliminary study also shows that the (100)CoGa/GaAs diode is electrically stable under a 500 °C, 20 min annealing.[10] In this article, we study the Schottky barrier height of CoGa diodes with different phases, and further we demonstrate the control of the Fermi pinning position by preconditioning the GaAs surface. Finally, the plausible mechanism for the change of the SBH is discussed.

II. EXPERIMENTAL

The n^+-(100)GaAs (Si-doped, 2×10^{18} cm^{-3}) was used for substrate in this study. A 4000 Å GaAs buffer layer with a Si-doping density between 8×10^{16} and 2×10^{17} cm^{-3} was grown by a standard MBE technique. CoGa of about 700–1000 Å thick was deposited under an ultrahigh vacuum (UHV) environment. In the growth of CoGa, the Co flux used was about 0.3 Å/s, and the Ga flux was equivalent to a GaAs growth rate of 0.4 μm/h, and the

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Schottky barrier of epitaxial (100)CoGa on GaAs

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Schottky barrier heights in the epitaxial (100) CoGa/*n*-(100) GaAs diodes were studied by the *I-V* and internal photoemission methods. Diodes of these epitaxial contacts were shown to exhibit good rectifying behaviors and the forward current was found to follow the thermionic emission theory. Using the temperature dependence of the barrier heights, we show that the Schottky barrier heights are about 0.67 eV by *I-V* and 0.68 eV by internal photoemission measurements. The Schottky barrier height was found to be constant for contacting to *n*-type GaAs in the temperature range between 150 and 300 K. From this fact, we conclude that the metal Fermi level is pinned relatively to the GaAs conduction band minimum in this case. This finding is similar to other epitaxial contacting cases, $CoSi_2$/Si and $ErSi_2$/Si, where the Fermi level pins to the nearest semiconductor band [J. Y. Duboz, P. A. Badoz, F. Arnaud d'Avitaya, and E. Rosenche, Phys. Rev. B **40**, 10 607 (1989)].

The metal–semiconductor interface is an important subject for ohmic and Schottky contacts. However, the Schottky barrier formation itself remains a challenging topic after decades of research because of the poor reproducibility of the experimental data and the inconsistency of the models for Fermi level pinning. There are many models developed for explaining the Fermi level pinning. One model says that the pinning is due to the interface chemical reactivity between metal and semiconductor.[1] Another model for the pinning phenomenon is the effective work function of several patchy contacts.[2] Other models argue that the pinning is associated with the semiconductor alone and are related to the metal-induced gap states,[3,4] or the intrinsic atomic vacancies (defects),[5] or antisite defects[6] at or near the semiconductor surface. However, to date no single theory can account for all the experimental data, and new experimental results will continue to shed light on this old problem. The central issue is that there are reactions between metal and semiconductor for most contacts, and the contacts may be in form of patches of contacts in a microscopic picture. For detailed understanding, a homogeneous interface with no reaction between the metal and GaAs is desirable. In this article, we present the data of an epitaxial CoGa/GaAs contact grown *in situ* by MBE. The use of the *in situ* growth method will provide a contamination-free GaAs surface and an intimate metal contact. The intermetallic compound (100)CoGa/(100)GaAs contact is chosen because this compound can be epitaxially grown on GaAs by MBE. Furthermore, Baugh *et al.* have already demonstrated that (100)CoGa/(100)GaAs is thermodynamically stable upon annealing up to 700 °C,[7] and this stability is a crucial advantage in device fabrication.

The crystalline quality of the epitaxial CoGa is verified by *in situ* RHEED (reflection high energy electron diffraction) patterns, two-theta x-ray diffraction, RBS (Rutherford backscattering), and x-ray rocking curves. The detailed discussion of the growth technique is published elsewhere.[8,9] The cross section TEM (transmission electron microscopy) image of the CoGa/GaAs interface is shown in Fig. 1. We can see from the picture that the CoGa is epitaxially grown on GaAs and the contact is intimate without observable reaction between CoGa and GaAs. Furthermore, the interface is abrupt and atomically smooth. For the Schottky barrier study, the (100)GaAs substrate is a n^+ Si-doped wafer with a doping density about 2×10^{18} cm^{-3}. The sample is indium-mounted on the holder, and this indium also serves as the backside ohmic contact for the Schottky diodes. A 4000 Å GaAs buffer layer with a Si-doping density of 8×10^{16} cm^{-3} is grown after the oxide layer is removed. Approximately one monolayer of Co is deposited before the growth of CoGa, a 1000 Å (100)CoGa is then grown onto the substrate. The growth temperature is kept at 300 °C to avoid the three-dimensional growth of the initial layers and also to prevent the interface reaction. After the growth, two different size diodes, 0.25 and 0.50 mm in diameters, are fabricated in mesa form, and then current-voltage (*I-V*), capacitance-voltage (*C-V*), and internal photoemission measurements are performed at different temperatures on these diodes.

The *I-V* equation of the thermionic emission current is as follows:

$$I=I_s\exp(qV/nkT)[1-\exp(-qV/kT)] \tag{1}$$

where I_s is the saturation current,

$$I_s=SA^*T^2\exp(-q\phi_b/kT). \tag{2}$$

Here, S is the electric contact area, A^* is the Richardson constant, ϕ_b is the Schottky barrier height, and n is the ideality factor. For $V>3kT/q$, the $[1-\exp(-qV/kT)]$ term becomes unity in Eq. (1). The measured *J-V* curves at room temperature for these Schottky diodes are shown in Fig. 2 for both the 0.25 and 0.50 mm diodes. The linear parts of these curves extend over five decades from 10^{-5} to 1 A/cm^2, indicating the merit of the use of the low resistivity substrate and also the good quality of the backside

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Organometallic vapor phase epitaxy of CoGa on (100)GaAs

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We report the first epitaxial growth of CoGa thin films on (100)GaAs substrates by organometallic chemical vapor deposition. The separate sources $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and Et_3Ga were mixed in a stream of carrier gas and decomposed in a conventional cold wall epitaxial reactor between 260 and 300 °C under atmospheric pressure. A typical growth rate of 1 μm/h was achieved and the film composition could be directly monitored from the gas phase composition. The Co-rich films have the α-Co metal structure and react with GaAs at 500 °C to form CoAs. By contrast, Ga-rich β-CoGa films were lattice matched on (100)GaAs and were found to be thermodynamically stable at 500 °C. This work demonstrates that organometallic vapor phase epitaxy is also a suitable technique for the fabrication of buried metal/semiconductor heterostructures.

In order to make new and useful electronic devices for the III/V semiconductors based on buried metal/semiconductor heterostructures, it is necessary to find metals which are both thermodynamically stable as well as lattice matched to these materials.[1–3] Transition metal gallides and aluminides have attracted a growing interest because they are thermodynamically stable[4–6] and they have a cubic structure with a lattice constant close to half the lattice constant of GaAs.[7] These intermetallic phases have been formed using physical deposition techniques such as evaporation[8] or molecular beam epitaxy (MBE), e.g., CoAl,[1] NiAl,[2,3] and CoGa.[6,9,10] However, organometallic vapor phase epitaxy technique (OMVPE), which is conventionally used for the deposition of the III-V layers, has several attractive advantages such as its versatility and suitability for large scale production applications.[11] Previously, we have reported on the polycrystalline deposition of one of such thermodynamically stable metals in a hot wall chemical vapor deposition (CVD) reactor, namely, the compound CoGa, from the single source precursor $(OC)_4CoGaCl_2(THF)$, **1**.[12] However, this intermetallic phase exists over a wide range of composition[13] and both the best lattice match and the highest thermodynamic stability occur for Ga-rich compositions of 61 at. % Ga[6] and 55 at. % Ga,[14] respectively. Here we wish to report on the successful epitaxial growth of CoGa films on (100)GaAs using the separate sources $(\eta^5\text{-}C_5H_5)Co(CO)_2$, **2**, and Et_3Ga, **3**, in a cold wall laminar flow reactor equipped with external focused infrared lamp; the compounds were purchased from Strem Chemical (Newburyport, MA).

The compound **2** was selected because it is a liquid; its vapor pressure, measured by the transport method in the temperature range 293–413 K, fits the equation:

$$\log p(\text{h Pa}) = 10.11 - 2971.8/T(\text{K}).$$

The vapor pressure of Et_3Ga was temperature controlled according to literature data.[15] Each organometallic precursor was contained in a thermostated Pyrex glass bubbler. Purified He was used as carrier gas for 2 to prevent premature decomposition in the bubbler whereas purified H_2 was used both for the transport of **3** and dilution of the gas streams at the entrance of the reactor. The reactor was a horizontal air-cooled quartz tube. The deposition temperature was monitored with a thermocouple imbedded in the heart of a refractory steel block on which the substrates were placed. The substrates and typical deposition parameters are reported in Table I. The substrates were placed into the reactor immediately after cleaning and subjected to several vacuum (10^{-3} h Pa)/H_2 cycles. They were then heated a few minutes at 300 °C under H_2 stream, the desired parameters adjusted, and the flow of **3** and **2** introduced in this order. At the end of the run the substrate temperature was decreased with a cooling rate of 2–3 °C/min to avoid a peeling off of the film due to thermal strains. The CoGa films were deposited under atmospheric pressure in the temperature range 260–300 °C. The composition of the films on (100)Si and Al_2O_3 (where interference from GaAs is absent) was determined by energy dispersive x-ray analysis (EDX) using a $Co_{0.5}Ga_{0.5}$ bulk sample as a standard; the composition of deposits on GaAs were analyzed by x-ray photoelectron spectroscopy (XPS). The Co/Ga atomic ratio in the films on (100)Si and Al_2O_3 agreed within 7% of that on GaAs.

As shown in Fig. 1, the Ga content of the film increases with the mole fraction of Et_3Ga up to 64 at. %, which is the upper limit of the β-CoGa phase as dictated by the phase diagram.[13] All deposition conditions were kept constant at two different temperatures, 260 and 300 °C; the film composition is weakly dependent on the deposition temperature. Alternatively, the Ga content of the film can be decreased by increasing the molar fraction of **2**, keeping constant the mole fraction of **3**.

Scanning electron microscopy (SEM) observations have revealed a smooth mirrorlike surface for the films grown on (100)GaAs substrates. The growth rate, determined from thickness measurements on cleaved GaAs and Si samples, is almost independent of the temperature (typically ~1 μm/h) for Et_3Ga (**3**) mol fraction of 2.6×10^{-3}. This and other data indicate that for high concentration of

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Variation of the Schottky barrier height of the differently oriented CoGa on GaAs by molecular beam epitaxy

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The Schottky barrier formation of CoGa on (100)*n*-GaAs is investigated. CoGa is grown by molecular beam epitaxy and the epitaxial orientation is controlled by the initial growth conditions of the GaAs substrate. Schottky diodes with three different phases of CoGa: (100)CoGa, (110)CoGa, and mixed (100) and (110)CoGa, are fabricated and Schottky barrier heights are measured by *I-V*, *C-V*, and internal photoemission. The fact that these three types of diodes have different values of barrier height indicates that the mechanisms of the barrier formation for these three phases are different. Finally, the temperature dependence of the Schottky barrier height is also examined and the barrier height is found to be constant from 150 to 300 K for each of the phases.

The metal/GaAs interface is an important subject for Ohmic and Schottky contacts. The ability to control the Schottky barrier height (SBH) will provide advantageous manipulation in device applications. However, the SBH for an ordinary metal contact on GaAs is known to pin at the mid-band gap of GaAs, independent of the metal work function. This pinning problem severely limits the flexibility of changing Schottky barrier height for many device applications. The mechanism for the pinning is not yet well understood, though many theories have been proposed to explain this phenomenon. However, to date no single theory can account for all of the experimental data. New experimental results will continue to shed light on this old problem.

The intermetallic compound, CoGa, is chosen as the contact metal on *n*-(100)GaAs in our study. Previously, the successful growth of epitaxial CoGa on GaAs has been demonstrated.[1] Baugh *et al.* have already demonstrated that (100)CoGa/(100)GaAs is thermodynamically stable upon annealing up to 700 °C.[2] A preliminary study also shows that the (100)CoGa/GaAs diode is electrically stable under a 500 °C, 20 min annealing.[3] In this letter, we study the Schottky barrier height of CoGa diodes of different phases. We further demonstrate the control of the Fermi pinning position by preconditioning the GaAs surface. Finally, the plausible mechanism for the change of the SBH is discussed.

The substrate used in this study is n^+-(100)GaAs(Si-doped, 2×10^{18} cm^{-3}). A 4000 Å GaAs buffer layer with a Si-doping density of between 8×10^{16} and 2×10^{17} cm^{-3} is grown by a standard molecular beam epitaxy (MBE) technique. Then, a 700–1000 Å CoGa layer is grown at 300 °C in UHV (ultrahigh vacuum) environment. When the Co and Ga shutters are opened simultaneously in depositing the film onto the As-$c(4\times4)$ substrate, a mixed phase of (100)CoGa and (110)CoGa is formed. To form the single phase (100)CoGa, approximately one monolayer of Co is deposited before the simultaneous deposition of Co and Ga. On the other hand, to achieve the single phase (110)CoGa, a small amount of Ga is deposited first, changing the surface reconstruction of the GaAs substrate from $c(4\times4)$ to Ga(4×6) or other Ga-rich surfaces. The predeposited Ga is about 1 Å thick (less than one monolayer); if too much Ga is deposited, however, the crystalline quality of the (110)CoGa degrades as revealed by the change of the reflection high-energy electron diffraction (RHEED) pattern. Consequently, a careful control of the initial growth condition of the substrate is essential in order to obtain the desired phase. The detailed description of the growth technique has been published elsewhere.[4]

The forward *I-V* curves of diodes with these three different CoGa phases at room temperature are shown in Fig. 1 (0.25 mm in diameter). In order to determine the SBH, we use the thermionic emission current formula

$$I=I_s\exp(qV/nkT)[1-\exp(-qV/kT)], \tag{1}$$

where I_s is the saturation current,

$$I_s=SA^*T^2\exp(-q\phi_B/kT). \tag{2}$$

Here, S is the electric contact area, A^* is the Richardson constant, ϕ_B is the Schottky barrier height, and n is the

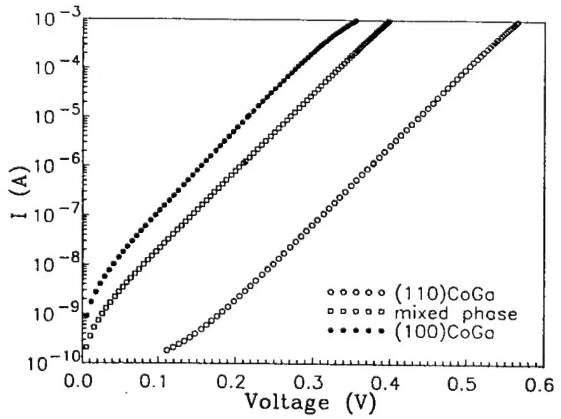

FIG. 1. Room temperature forward *I-V* curves of CoGa diodes with the three different phases: (100)CoGa, (110)CoGa, and mix of (100) and (110). The diameter of these diodes is 0.25 mm.

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Epitaxial Growth of CoGa on GaAs by Organometallic Chemical Vapor Deposition

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Epitaxial layers of CoGa have been grown successfully for the first time on (100)GaAs by organometallic chemical vapor deposition, using $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and Et_3Ga as precursors. The composition of the intermetallic films is adjustable by control of the composition of the gas phase in such a way that no detectable lattice mismatch is observed between Ga-rich CoGa films and the GaAs substrate. However, the films deposited with an excess of Co exhibit a metastable α (fcc) structure corresponding to a $Co_{1-x}Ga_x$ solid solution. These films are structurally incompatible with GaAs, and were also found to react with GaAs above 400 °C to form CoAs. From gas phase compositions $Et_3Ga/CoCp(CO)_2 \geq 1$ the CoGa films have the cubic β (CsCl) structure and grow epitaxially on (100)GaAs in the temperature range 260–300 °C. The growth rate of these films has been investigated as a function of the deposition parameters. The Ga-rich β-CoGa films are thermodynamically stable on GaAs at 500 °C, which is the temperature used for GaAs epitaxial growth by this technique. This suggests that CoGa is a good candidate material for the fabrication of buried metal/GaAs heterostructures by organometallic vapor-phase epitaxy.

Introduction

Contact metallization is currently a limiting factor in III–V semiconductor device technology. This is because most single element metals are thermodynamically unstable with respect to III–V semiconductor such as GaAs. Chemical reactions at metal/semiconductor interfaces lead to changes in the electrical properties of the contact. To avoid this instability, the metallic film should be thermodynamically stable toward the semiconductor compound. From this point of view, the metal–III–V ternary phase diagrams provide a useful framework for the selection of the metallization materials.[1]

Furthermore, if a single-crystalline metallic film is grown epitaxially on the semiconductor, the stability of the interface will be improved, and it will possible to grow an additional semiconductor epilayer on top. Metals which are both thermodynamically stable and lattice matched to the semiconductor will allow the preparation of new and useful electronic devices based on buried metal/semiconductor heterostructures, as was recently demonstrated for metal alumide/semiconductor systems.[2–5]

Transition metal gallides and aluminides have attracted a growing interest because they are both thermodynamically stable[6–8] and have a cubic structure (CsCl, B2 type) with a lattice constant close to half the lattice constant of GaAs.[9] Epitaxial growth of these intermetallic phases was successfully achieved by physical deposition techniques such as evaporation followed by annealing, e.g., CoGa/GaAs,[10] NiAl/GaAs,[11] and PtAl/GaAs[12] or directly by molecular beam epitaxy (MBE), e.g., CoAl,[2,13] NiAl,[3–5] CoGa,[14–19] NiGa,[20] RhGa,[21] PtGa,[22] and $AuGa_2$.[23] The suitability of rare-earth arsenides for epitaxial metallization was also investigated by MBE, e.g., ErAs,[24,25] LuAs,[25] and YbAs,[26] as well as metal arsenide, Rh_2As.[27]

However, the organometallic vapor-phase epitaxy technique (OMVPE), which is conventionally used for the deposition of the III–V layers, has several attractive advantages over physical deposition techniques such as its versatility and suitability for large-scale production

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Ballistic-electron-emission microscopy of (100)CoGa/*n*-type GaAs interfaces grown by molecular beam epitaxy

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A scanning tunneling microscope (STM) was used for the first time to investigate the (100)CoGa/GaAs interfaces grown by molecular beam epitaxy. The surface image indicates a vertical variation of about 7.5 Å with some domains of dimensions of about 170 Å. Furthermore, ballistic-electron-emission-microscopy spectra of this metal/semiconductor interface show two turn-on voltages, which account for the change of transmission probabilities for electrons with energies above the L minima and X minima of GaAs, respectively. The transmission into the X valleys of GaAs is found to be relatively stronger than that into the L valleys. This is explained by the CoGa band structure and the conservation of energy and transverse momentum for ballistically injected electrons. So far no ballistic electron current flowing into the Γ valley has been observed. For this reason, Schottky barrier height and its spatial variation measured by STM were not directly from the anticipated turn-on voltage at the Γ minimum, but instead, from the thresholds corresponding to transmission into higher valleys.

Epitaxial metal/semiconductor interfaces have received increased attention in recent years for their potential applications such as metal contacts, and metal-base[1] and permeable-base[2] transistors. A great deal of progress has been made due to the improvement of the growth technique, especially in the molecular-beam-epitaxy (MBE) growth. In addition to the improvement of preparation of near ideal contacts, one other direction is to study the microscopic picture of the Schottky barrier behavior. Recently, Kaiser *et al.* have used ballistic electron emission microscopy (BEEM) measurement to study the Schottky barrier height (SBH) of the Au/GaAs interface with spatial resolution on the nanometer scale.[3] The use of BEEM technique provides several advantages compared with the conventional methods of current-voltage (I-V), capacitance-voltage (C-V), and internal photoemission spectroscopy (IPS) measurements. In addition to spatial resolution of SBH variation, BEEM yields information on interface transport and interface band structure, with a scanning tunneling microscope (STM). The recent success of the epitaxial metal contact grown on GaAs has made the BEEM measurement even more interesting. The epitaxial contact provides a smooth and reaction-free interface for the SBH studies and BEEM can help in further understanding the interface.

The CoGa/GaAs(100) interface has been of particular interest because of its high crystal quality and thermodynamical stability. The lattice mismatch of CoGa with GaAs is from 1.8% to 0.5% for Ga content ranging from 31% to 61%, the maximal stoichiometry variation allowable for growth of single phase CoGa on GaAs.[4] An abrupt and reaction-free epitaxial contact has been demonstrated from the transmission electron microscopy and reflection high energy electron diffraction patterns by Kuo *et al.*[4,5] Furthermore, some electronic properties such as surface stance and SBH have been studied for two epitaxial directions, (100) and (110).[6,7] However, no assessment of the surface quality and spatial variation on SBH have been made in the past. In this letter, we report the STM and BEEM data of the epitaxial (100)CoGa/(100)GaAs contact for the first time.

In this study, CoGa overlayers were grown on a 3500 Å (100)GaAs buffer layer (Si-doped, $\sim 1\times 10^{17}$ cm^{-3}) by MBE and the growth procedure was described elsewhere.[4] A n^+(100)GaAs with a Si-doping density of about 1×10^{18} cm^{-3} was used as the substrate. A STM system setup with a platinum tip operating in air was used for the investigation of the Schottky barrier system of the CoGa/GaAs interface. The scan motion of the tip was calibrated by taking the image of a piece of pyrolytic graphite, for which the lattice constant is well known. Also prior to the study of the CoGa/GaAs interface, a BEEM measurement on Au/Si interface was performed with this STM system, which yielded the same threshold voltage as reported by Kaiser *et al.*[3] The results reported in this letter were obtained at a working temperature of 25 °C.

Before each BEEM measurement, the CoGa surface was imaged by the STM system to ensure a smooth surface around the measured area. For a ~35 Å CoGa film, the vertical variation in an 800 Å×800 Å region is as small as 7.5 Å, as shown in Fig. 1(a), about the thickness of three to four atomic layers. Some monolayer domains formed surface ripples for which the sizes are estimated to range from 160 to 180 Å. In contrast, for a 500 Å (100)CoGa film grown in the same conditions on GaAs, the surface image is shown in Fig. 1(b).

BEEM experiments were performed for the 35 Å film only. The BEEM curve and its derivative, as shown in Figs. 2(a) and 2(b), show a turn-on voltage of ~1 V and an increase in slope at ~1.2 V. Following the treatments for locating the threshold voltages, V_b's of the BEEM curves in the Au/GaAs case, the fit was obtained using the equation,[8]

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